PB-237 917-T

HYGIENIC AND TOXICOLOGICAL CHARACTERISTICS OF BREAKDOWN PRODUCTS OF PHENOL IN THE OZONE TREATMENT OF WATER

A. A. Korolev, et al

Environmental Protection Agency
Research Triangle Park, North Carolina

1973

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

312307

NTIS

PB 237 917-T

EPA-HS-178

HYGIENIC AND TOXICOLOGICAL CHARACTERISTICS OF BREAKDOWN PRODUCTS OF PHENOL IN THE OZONE TREATMENT OF WATER

(Gigienicheskaya i toksikologicheskaya kharakteristika produktov destruktsii fenola pri ozonirovanii vody)

A. A. Korolev, A. A. Abinder, M. V. Bogdanov,
T. A. Zakharova and N. K. Khitrov

Gigiena i Sanitariya, Vol. 38, No. 8,
pp. 6-10

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Translated for EPA by
SCITRAN (SCIENTIFIC TRANSLATION SERVICE)
SANTA BARBARA, CALIFORNIA

HYGIENIC AND TOXICOLOGICAL CHARACTERISTICS OF BREAKDOWN PRODUCTS OF PHENOL IN THE OZONE TREATMENT OF WATER

by

A. A. Korolev, A. A. Abinder, M. V. Bogdanov,
T. A. Zakharova and N. K. Khitrov

Department of Public Hygiene
I Moscow Medical Institute imeni I. M. Sechenov

The contamination of reservoirs with phenols and practically no barrier function of water purification equipment in relation to these compounds (S. N. Cherkinskiy et al.) necessitate the study not only of capability for oxidation during the purification of drinking water and sewage, but also the chemical nature and biological activity of breakdown products.

Data on the kinetics of oxidation of phenols by ozone (O_3) and the nature of breakdown products have been given previously by one of the authors of this article (A. A. Korolev). Evaluation of the toxicity of the oxidation products of phenols showed that weakly-oxidized solutions of hydroxinone do not differ from fresh preparations (Ye. A. Mozhayev et al.); the toxicity of 99% oxidized solutions of orcein is reduced 9 times (U. Kirso and I. Veldre). No attempt has been made to evaluate the toxicity of ozonation products of phenols. As the oxidation of phenols by O_3 occurs in several stages, we can assume the presence in these systems not only of products of advanced breakdown but also those of the initial oxidation of quinoid structure, which are capable of further reactions with the oxidant and have known biological activity. Therefore, we conducted experiments on warm-blooded animals with both unoxidized phenols and with products of the breakdown of phenols by O_3 in order to determine the degree of their toxicity and cumulativeness. The number of intact phenols was determined spectrophotometrically and colorimetrically with 4-amino-antipyrine.

The results of several series of acute tests on white mice with ozonized and non-ozonized 2-5% solutions of phenol, hydroxynone and pyrogallol are given in Table 1.

The table shows that solutions of phenols before treatment with O_3 were highly toxic; however, as the depth of oxidation and the accumulation of breakdown products increased, the toxicity of ozone-treated solutions progressively dropped. The clinical picture of acute poisoning of the animals by ozonized solutions did not depend on the degree of decomposition of the phenols and corresponded to symptoms of poisoning with the original substances. This in-

Table 1

The dynamics of LD_{50} of phenols depending on the degree of their breakdown by ozone

Substance	LD_{50} before ozone treatment (in mg/kg)	After ozone treatment			
		% of breakdown	LD_{50} (in mg/kg)	% of breakdown	LD_{50} (in mg/kg)
Phenol	270 (215-310)	25-28	355 (319-389)	60-63	650 (498-901)
Hydroxynone	245 (196-293)	40-48	485 (344-625)	82-88	1760 (1533-1980)
Pyrogallol	300 (228-371)	75-78	1750 (1546-1954)	--	--

dicated that with the administration of oxidized solutions, the death of the animals was caused by residual amounts of phenols, and breakdown products themselves are practically nontoxic in tested doses. This was verified by the results of a test with the administration of a 99% broken down solution of phenol to white mice in doses of 5000 mg/kg (converted to the original amount of the product); not one death was observed among the animals.

Taking into account the high sensitivity of amphibians to phenols, we conducted 2 series of tests on frogs in order to study the toxic effect of phenol and the products of its breakdown by O_3. The frogs were immobilized by severing the spinal cord; after the thoracico-abdominal wall was opened, we inserted into the ventricle of the heart a glass cannula, filled with a physiological solution and connected to the head of an induction electromanometer. After a stationary regime was established, 0.2 ml of a physiological solution containing phenol in a concentration of 100 mg/l and an analogous solution of phenol 63-68% broken down by O_3 were injected into the left ventricle. The effect was recorded by a multichannel polygraph manufactured by the "Nichen-Khoden" company and evaluated by the degree of reduction of the force of heart contractions, the character of change in the configuration of ventricular complexes on the EKG and variation in the frequency of heart contractions (Fig. 1).

With intra-auricular injection of phenol in a concentration of 100 mg/l, a sharp reduction was observed in the amplitude of intraventricular pressure against a background of normal heart contraction rate and lack of EKG changes. With the injection of a solution of phenol oxidized 63-68%, disturbances were noted in heart activity, similar in character, but significantly less severe. These data indicate that changes are due to residual amounts of unbrokendown phenol and the breakdown products of phenol by O_3 themselves are biologically inactive.

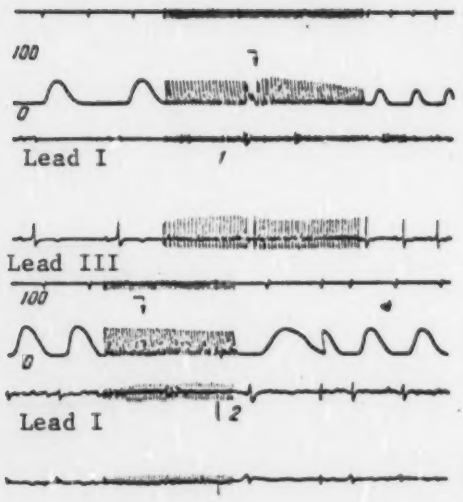

Figure 1. The effect of phenol and the products of its breakdown by ozone on contraction and electric activity of the ventricle of the heart of a frog.

From top to bottom: time mark (in seconds), pressure in the ventricle (in mm Hg), EKG in I and III standard leads. Arrows indicate the moment of introduction.

1 — the effect of the injection of a 0.2 ml solution of phenol in a concentration of 100 mg/l; 2 — the effect of the injection of a 0.2 ml solution of phenol in the same concentration but previously broken down 65% by ozone.

In experiments on rabbits, it was established that solutions of hydroxynone in concentrations of 50-100 mg/l, when injected in the amount of 3 ml into the outer vein of the ear of a rabbit, increased arterial pressure 40-60 mm, reduced heart rhythm 15-28% and caused individual extra systoles, but did not affect contractility of the myocardium of the left ventricle. With 83-90% breakdown of hydroxynone by O_3 in such solutions, the above described effect completely disappeared. Therefore, oxidation products of hydrozynone resulting from the effect of O_3 are also nontoxic and biologically inactive, as are the oxidation products of phenol.

To reveal the cumulative properties of phenols and their breakdown products resulting from the effect of O_3, two series of tests were conducted on white mice which in the course of 3 weeks received phenol in doses of 5 and 50 mg/kg and hydroxynone in doses of 20 and 100 mg/kg. Products of 90-92% oxidized solutions of phenol and hydroxynone were administered in these same

doses, converted to the initial compounds. In each series of tests,30 animals were used, divided into 5 groups, of which the first group served as the control and the other four received various doses of phenol, hydroxynone and their ozonation products.

To evaluate the functional state of test animals,observations were made of weight dynamics, peripheral blood, the activity of cholinesterase and peroxidase in the blood and aspartate-aminoferrase in urine as well as the amount of SH-groups in the blood. Posthumously determined were the mitotic activity of brain cells, the activity of cholinesterase in the liver and weight coefficients of internal organs. It was found that only with intoxication with non-ozonized phenol or hydroxynone in doses of 50 and 100 mg/kg, respectively, was the number of erythrocytes and the amount of hemoglobin increased, SH-groups decreased and the activity of aspartate-aminoferrase in the urine, cholinesterase and peroxidase in the blood and cholinesterase in liver homogenates increased. Weight coefficients of internal organs and the mitotic activity of brain cells were practically unchanged. The introduction of the products of the break down of phenol and hydroxynone with O_3 in all tested doses had no effect on any of the above listed indices. Therefore, ozonization products of phenol and hydroxynone are not only not toxic, but also practically non-cumulative.

Table 2

The dynamics of the breakdown of phenol, changes in odor and indices of bichromate oxidizability during ozone treatment

Indices	before ozone treatment	Doses of ozone					
		5 mg/1			10 mg/1		
		5 min.	10 min.	15 min.	5 min.	10 min.	15 min.
Concentration of phenol (in mg/1)	50.0 100.0	17.5 93.5	5.4 25.0	3.8 11.0	6.0 30.0	2.0 9.3	0.0 5.4
Dilution when odor disappears	1:50 1:100	1:10 1:80	1:5 1:20	1:2 1:10	1:5 1:20	1:2 1:10	0 1:5
Bichromate oxidizability (in mg/1 O_2)	85.0 175.0	54.5 100.0	39.5 87.5	25.0 60.0	42.0 91.5	23.5 68.5	9.0 41.5

Before termination of the experiment,daily urine samples were collected from the animals receiving different doses of phenol and its ozonization products and color intensity were evaluated. It was established that only in animals receiving non-ozonized substances in doses of 50 mg/kg was urine a brownish color because of the presence of significant amounts of free phenol. Lack of color in urine from animals injected with ozonized phenol in the same dosage can be the result of preliminary oxidation of phenol by O_3 in vitro which

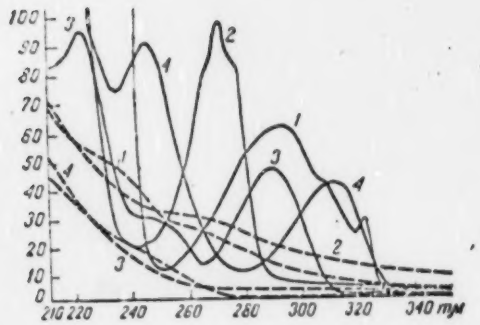

Figure 2. Spectral characteristics of solutions of phenols and their ozonization products.

Dashed lines — products of the breakdown of phenols by ozone; solid lines — the same phenols before ozonization; 1 — α-naphthol; 2 — phenol (oxybenzene); 3 — hydroxynone; 4 — 2,4.6-trichlorophenol.

somehow replaces a certain phase in the metabolism of this substance in vivo, thereby promoting deeper and quicker detoxification of the poison and its excretion with urine in the form of final, already colorless products. This mechanism, in all probability, also underlies the significant reduction of toxicit' of phenol after ozonization.

The ability of phenols, especially their chlorine derivatives, to alter the organoleptic properties of water, even in very slight concentrations, is well known (N. M. Svetlakova). Therefore, we gave a great deal of attention to changes during ozonization of the organoleptic properties of water contaminated by phenols. Part of the material is given in Table 2. It can be seen that increase in the degree of break down of phenol is paralleled by significant weakening of odor and reduction of bichromate oxidizability of the solutions. Complete break down of phenol and the disappearance of odor under the conditions of our test were observed with a ratio of 3-3.5 mg O_3 to 1 mg of phenol, which agrees highly with the data of Bauch et al.

Ozone treatment of solutions of 2,4-dichlorophenol and 2,4,6-trichlorophenol also showed the high effectiveness of this method. If dilution 2500-10,000 times is required to remove the odor of original solutions in concentration of 10 mg/l, after treatment with 7 mg/l of O_3 for 10 minutes, the odor had already disappeared with dilution 20-50 times.

Spectrophotometry of aqueous solutions of phenols, using the instrument made by the "Hitachi" company, showed that after ozone treatment, the "peaks" typical of phenol, hydroxynone, pyrogallol, 2,4,6-trichlorophenol, pyrogallol A and α and β-naphthols in the ultraviolet part of the spectrum disappear and slightly sloping lines of the same type for all these substances appear, whose degree of expression depended both on the dose of O_3 and on the time of contact (Fig. 2). The appearance of such lines serves as an indirect index that products of the break down of tested phenols by O_3 are similar in chemical nature. Therefore, there is the sound possibility of eliminating toxicological

tests with ozonization products of each individual phenol. It is sufficient to evaluate the degree of toxicity and the cumulativeness of oxidation products of any one phenol and extrapolate the data to other compounds of the same class.

Our experiments on animals completely confirmed, from a toxicological point of view, the correctness of the theory regarding the common properties of products of the break down of simple phenols by O_3.

Conclusions

1. All tested phenols are easily oxidized by ozone, as the result of which the organoleptic properties of water contaminated by these substances are significantly improved.

2. The products of advanced oxidation of phenols by ozone are practically nontoxic and noncumulative.

3. The ozonization method can be recommended for wide use to purify drinking water and sewage contaminated by phenols.

REFERENCES

1. Kirso, U. and I. Veldre. Izv. AN Estonsk.SSR. Seriya Khimiya. Geologiya, No. 1, 1971, p. 26.

2. Korolev, A.A. Gig. i san., No. 12, 1972, p. 78.

3. Mozhayev, Ye.A., V.P. Osintseva and Ye.V. Arzamastsev. Farmakol. i toksikol., No. 2, 1966, p. 236.

4. Svetlakova, M.N. The effect of various phenols on the organoleptic properties of water. Gig. i san., No. 2, 1955, p. 11.

5. Cherkinskiy, S.N., L.N. Gabrilevskaya and V.P. Laskina, et al. Ibid., No. 5, 1972, p. 12.

6. Bauch, H., H. Burchard and H.M. Arsovis. Gesundheits-ingenieur, No. 91, 1970, p. 258.